PATENT SPECIFICATION

(11) 1 592 802

1 592 802

(21) Application No. 40288/77 (22) Filed 28 Sept. 1977
(31) Convention Application No. 727934
(32) Filed 29 Sept. 1976
(31) Convention Application No. 727936
(32) Filed 29 Sept. 1976
(31) Convention Application No. 727673
(32) Filed 29 Sept. 1976 in
(33) United States of America (US)
(44) Complete Specification published 8 July 1981
(51) INT CL^3 C09C 3/12
(52) Index at acceptance
C1A 13 323 324 325 421 510 D1 D31 D41 D45 D8 G12 G12D41 G47 G47D45 G48 G48D1 G48D45 G4 G4D41 G4D8 J1 J203 J294 J321 J343 J580 M11 M1 N34 N4 VF1
B2E 1747 422T 438T 505S 506S 507S 508S 509S 511S 520S M

(19) THE PATENT OFFICE LONDON

(54) SILANE TREATED SURFACES

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United Sates of America, whose registered office is, 270 Park Avenue, New York, State of New York 10017, United States of America, (assignee of SIDNEY ETHAN BERGER and GEORGE ANTHONY SLENSKY), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to organosilicon treated particulate materials in which the organo group contains polyether groups. More particularly, this invention is concerned with organosilicon treated inorganic particulate materials readily employable in coating compositions, plastic molding compositions and in reinforced plastic composite compositions.

Organosilicon compounds have for some time been employed in the treatment of inorganic oxide surfaces such as inorganic oxide films, particulate fillers and pigments, and fibers (such as glass fibers, aluminum fibers and steel fibers). Aluminum and steel fibers are regarded to be oxide surfaces because they are oxidized even though their subsurfaces are not. The typical organosilicon treatment involves coating such surfaces with a hydrolyzate (and/or condensate of the hydrolyzate) of an organofunctional hydrolyzable silane. Such organofunctional hydrolyzable silanes are termed "Coupling Agent" and/or "Adhesion Promoter". The organofunctional groups typically contain groups reactive with complimentarily reactive groups in the medium in which the Coupling Agent is provided. The Coupling Agent is typically supplied to the surface of the inorganic oxide whereby through the hydrolyzable groups or silanol groups (≡Si—OH), bonding through siloxy moieties (≡Si—O—) is effected. Typical hydrolyzable groups include alkoxy of 1 to 4 carbon atoms, alkoxyalkoxy containing up to 6 carbon atoms, halogen such as chlorine, fluorine, and bromine, acyloxy of 2 to 4 carbon atoms, phenoxy, and oxime. The preferred hydrolyzable groups are alkoxy, alkoxyalkoxy and acyloxy. Common organofunctional groups are bonded to silicon by a carbon to silicon bond. The typical commerical functional radicals present in the organofunctional groups are vinyl, methacryloxy, primary amino, beta-aminoethylamino, glycidyl, epoxycyclohexyl, mercapto, polysulfide, ureido, and polyazamide. Another conventional technique for supplying the Coupling Agent to the inorganic oxide surface is by the integral blending technique. This technique involves adding to the resin medium the desired amount of the Coupling Agent and providing the medium in contact with the inorganic oxide surface by supplying the latter as a particulate filler or fiber to the medium or supplying the medium with the Coupling Agent to a continuous surface in the form of a film, fabric, foil or other shapes, wherein the Coupling Agent migrates within the medium to contact the surface or surfaces, react thereat and couple with the medium under the molding, curing, and other shaping conditions.

As a rule, Coupling Agents, enhance the chemical bonding between the

medium and the inorganic oxide substrate whereby to achieve improved adhesion between them. This could affect the strength properties of the composite of the plastic or resin associated with the inorganic oxide substrate or substrates.

Apart from use of organofunctional silanes as Coupling Agents, they have been used, in selected cases, as fiber and fabric sizing agents and as pigment modifiers to alter dispersion characteristics in a given medium. Illustrative of these utilities, polyazamide silanes as disclosed in U.S. 3,746,748, patented July 17, 1973, are effective sizes for glass fiber woven fabrics, and methylsilanes have been employed to modify the dispersion characteristics of silica aerogels in silicone rubbers minimizing creep hardening of the silicone gum undergoing cure. The methyl groups in this case may be functional because the cure mechanism may attack them.

Silane Coupling Agents have been extensively employed in the surface treatment of inorganic particulate materials such as fillers, pigments, and materials which also act to reinforce the resin or plastic material in which it is incorporated such as asbestos fibers and relatively short length glass fibers, such as staple glass fibers. All of these have been beneficially treated by certain organofunctional silane Coupling Agents. However, in only rare instances do these Coupling Agents provide benefits other than increased adhesion. One particular exception is the use of vinyl silanes on aluminum trihydrate to enhance, to a limited degree, their dispersion in polyester resin systems. It is traditionally accepted that organosilanes add essentially no benefits to and generally detract from the properties of carbon black when employed in paints, dyes, rubber, plastics, etc., even though carbon black contains chemisorbed oxygen.

There is described herein the use of an organosilane which is relatively non-reactive in its organo moiety and has the capability of reacting with inorganic oxide surfaces (including carbon black) to which it is supplied. This silane, by virtue of the relative inactivity of its organic moiety, should not be classically termed a Coupling Agent, yet its utilization on inorganic particulate materials results, in many cases, in improved strength properties for the composite in which it is incorporated. However, the main feature of this organosilane is the fact that it provides to the particulate inorganic oxide, to which it is supplied, superior properties in the area of handling when utilized in the manufacture of a composite system. This organosilane contains polyether moieties which are essentially non-reactive in terms of their ability to covalently bond to functional or nonfunctional plastic or resinous materials, yet it does possess the capability of associatively bonding, as well as provide a measure of compatibility, with the resin or plastic system in which the particulate inorganic oxide containing it is to be supplied.

According to the present invention there is provided a composition comprising inorganic oxide particles (as hereinbefore defined) containing on their surfaces a silane, its hydrolyzates or resulting condensate, which silane has the following general formula:

$$R''\text{—}(\text{—}OR'\text{—})_a\text{—}ORSiX_3 \qquad (I)$$

wherein R can be any divalent organic group which is either oxygen or carbon bonded to the silicon atom; R' is one or more 1,2-alkylene groups each containing at least 2 carbon atoms; R'' is hydrogen, an alkyl group containing 1 to 8 carbon atoms, an acyloxy group containing 2 to 4 carbon atoms or an organofunctional group; X is a hydrolyzable group; and a has an average value of 4 to 150.

One embodiment of the invention relates to the treatment of particulate titanium dioxide with the organosilane described herein which serves to enhance its employment in pigmented and/or filled paints and plastics, and in reinforced plastic composite compositions.

It should be understood that the use of the organosilane described herein to treat particulate inorganic oxide materials is not limited merely to the treatment of titanium oxide. Other aspects and embodiments of the invention will become apparent from the disclosures herein.

The organosilanes of this invention are characterized as structures having the following general formula:

$$R''\text{—}(\text{—}OR'\text{—})_a\text{—}ORSiX_3 \qquad (I)$$

R in Formula (I) can be any divalent organic group which is either oxygen or carbon bonded to the silicon atom.

R may be any divalent radical which effectively joins the remainder of the molecule to the silicon atom. In essence, R is an inert moiety of the invention because the invention contemplates two components joined together into one molecule. The first component is a hydrolyzable group characterized by the moiety —SiX_3 and the second component is the group characterized by the moiety —(—OR^{I}—)$_a$—. Though typically the relationship of the two moieties to each other in the classical sense of Coupling Agents, assuming the —(—OR^{I}—)$_a$— moiety was termed organofunctional, would be dependent upon the size and chemical characterization of "R", that relationship is not apparent in the case of the present invention. Thus given a particular "R", there exists an —(—OR^{I}—)$_a$— and a —SiX_3 combination which provides the advantages of this invention.

Usually, when R is an extremely large or bulky moiety, its impact upon the utility of the organosilane of formula (I) can be mitigated by increasing the size of *a* and/or using a solvent, such as ethanol, when the silane is supplied to the inorganic oxide.

Though other desirable R's will be illustrated hereinafter, the preferred R is an alkylene group containing from 1 to 8 carbon atoms, preferably 2 to 6 carbon atoms. R^{I} is one or more 1,2-alkylene groups each containing at least 2 carbon atoms and typically not more than 4 carbon atoms, preferably R^{I} is ethylene. R^{II} is hydrogen, an alkyl group containing 1 to 8 carbon atoms, preferably 1 to 4 carbon atoms, acyloxy (of 2 to 4 carbon atoms) or an organo-functional group such as the examples of organofunctional groups given below for R^{3}, X is a hydrolyzable group such as alkoxy containing, for example, 1 to 4 carbon atoms, alkoxyalkoxy in which the terminal alkyl contains 1 to 4 carbon atoms and the internal alkyl is alkylene which contains 2 to about 4 carbon atoms and is preferably ethylene; acyloxy such as acetoxy or propionoxy; aryloxy such as phenoxy, para-methylphenoxy; oximes; calcium oxide, sodium oxide or potassium oxide. In formula (I), *a* is a number having an average value of 4 to 150, preferably 4 to 120.

The silane of formula (I) as a preferred embodiment is described in U.S. Patent No. 2,846,458, patented August 5, 1958. A particular illustration of that silane is set forth at Column 3, line 20, et sequence, of the aforestated patent. However, this invention is not to be construed as limited to the particular silanes which are described in the patent. For example, the patent is exceedingly restrictive in terms of the description of the divalent organic group which joins the polyether to the silicon atom. In accordance with this invention that divalent organic group encompasses a much greater class of moieties.

Illustrative of the expanse of moieties encompassed by *R* above, are the following:

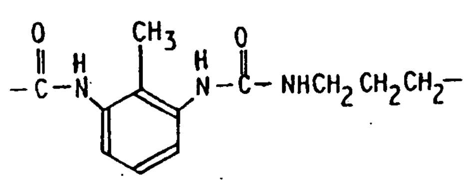
—$CH_2CH_2CH_2$—;

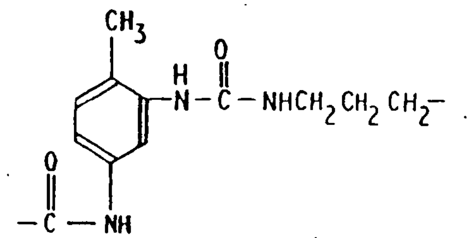
—CH_2CH_2—;

$$—\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2—;$$

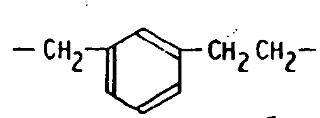
$$—(—CH_2\underset{\displaystyle (CH)_y}{\underset{|}{CH_x}}—O—)_c—,$$

wherein *c* is 1 to 20, *x* is 1 when *y* is 1 and 2 when *y* is 0, and *y* is 0 or 1;





$—CH_2CH_2CH_2SCH_2CH_2CH_2—$; and



As can be seen from the above, the characterization of R is exceedingly diverse and its ultimate limits have not been ascertained except insofar as all experimental evidence has indicated that it constitutes a basically inert component as compared to the function of the hydrolyzable silicon moiety and the separate polyether moiety as characterized above.

Illustrative of the $—(—OR^{I}—)_a—$ moiety of the silanes of formula (I) is the following:

$$—(—OR^{III}—)_p— —(—OR^{IV}—)_q—$$

in which R^{III} and R^{IV} are different 1,2-alkylene radicals, in which R^{III} is ethylene and R^{IV} is 1,2-propylene or 1,2-butylene, p is a number greater than q and the sum of p and q is equal to the value of a.

The silanes of formula (I) may be used alone or in combination with another and different silane, such as one encompassed by formula:

$$R^3_n(SiX_{4-n})_b \qquad \text{(II)}$$

or the cohydrolyzate or the cocondensate of such silane with that of Formula (I) above. In formula (II), n is equal to 0 or 1 and R^3 is an organic radical whose free valence is equal to the value of b and can be alkyl group of 1 to 18 carbon atoms, preferably 3 to 14 carbon atoms, or an organofunctional group bonded to silicon by a carbon to silicon bond. The organofunctional group thereof may for example, be one or more of the following groups; vinyl, methacryloxymethyl, gamma-methacryloxypropyl, aminomethyl, beta-aminopropyl, gamma-aminopropyl, delta-aminobutyl, beta-mercaptoethyl, gamma-mercaptopropyl, gamma-glycidoxypropyl, beta-(3,4-epoxycyclohexyl)ethyl, gamma-chloroisobutyl, polyazamides such as described in U.S. Patent No. 3,746,348, gamma - (beta - aminoethyl) - aminopropyl, (ethylene beta-aminoethyl) methacryl ammonium hydrohalide and beta - (4 - vinylbenzyl) (ethylene - beta - aminoethyl) ammonium hydrohalide. Any organo functional hydrolyzable silane suitable for use as a Coupling Agent may be employed in combination with the silane of formula (I). In formula (II), b is a positive number, generally 1 and typically not greater than 5, and X is the same as described for formula (I).

When there is employed a combination of or coreaction products of the silanes of formulae (I) and (II), the amount of silane of formula (I) employed should be that amount which provides a viscosity reduction and other advantages as hereindefined. Any amount of the silane of formula (II) may be employed so long as such does not hinder the role of the silane of formula (I).

The silane of formula (I) can be separately employed with the silane of formula (II). For example, they can both be applied neat or from aqueous solution to the substrate simultaneously or in sequence, or they can be premixed and supplied to the treated surface together as a mixture or co-reaction product. The maximum amount of reaction of the silanes is less than that amount of condensation from the hydrolysis products which renders the condensation product insoluble in an aqueous solution which may or may not contain a water soluble solvent such as ethanol.

Illustrative of the diversity of organosilanes covered by formula (I) are the following:

$H_3CO(CH_2CH_2O)_4CH_2CH_2CH_2Si(OCH_2CH_2OCH_2CH_3)_3$

$H_3CO(CH_2CH_2O)_{7.5}CH_2CH_2CH_2Si(OCH_3)_3$

$CH_3\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_8CH_2CH_2CH_2Si(OCH_3)_3$

$CH_2{=}\underset{}{\overset{CH_3}{\overset{|}{C}}}{-}\overset{O}{\overset{\|}{C}}{-}O(CH_2CH_2O)_{12}CH_2CH_2CH_2Si(OCH_3)_3$

$HO{-}({-}CH_2CH_2O{-})_{13.2}{-}CH_2\overset{OH}{\overset{|}{C}}HCH_2OCH_2CH_2CH_2Si(OCH_2CH_2OCH_3)_3$

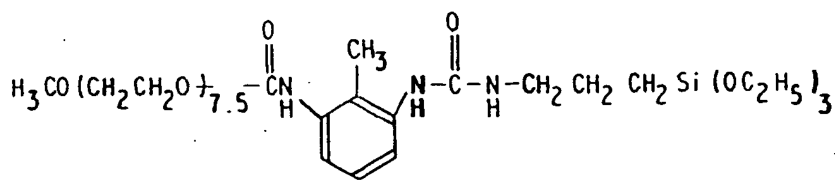
$H_3CO{-}({-}CH_2CH_2O{-})_{113}{-}CH_2CH_2CH_2Si(OCH_3)_3$

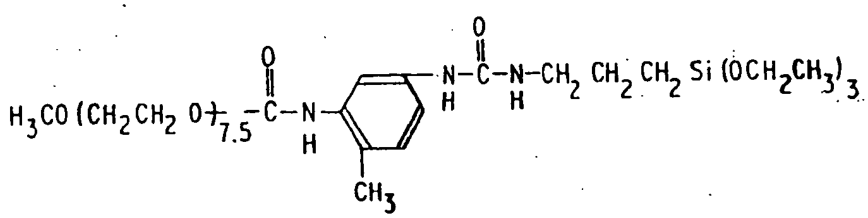
$[HO(CH_2CH_2O{-})_4{-}]_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3$

$CH_3O{-}({-}CH_2CH_2O{-})_{20}{-}({-}CH_2\underset{CH_3}{\underset{|}{C}}HO{-})_4{-}CH_2CH_2CH_2Si(OCH_3)_3$

$CH_3O{-}({-}CH_2CH_2O{-})_{70}{-}({-}CH_2\underset{CH_2CH_3}{\underset{|}{C}}HO{-})_5{-}CH_2CH_2Si(OCH_2CH_2CH_3)_3$

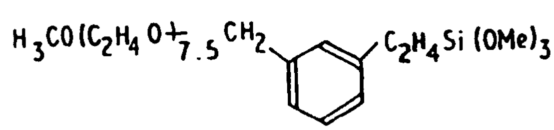
$CH_3CH_2O(CH_2CH_2O{-})_{32}{-}Si(OCH_2CH_3)_3$





$H_3CO(C_2H_4O{-})_{7.5}{-}\overset{O}{\overset{\|}{C}}\underset{H}{N}{-}C_3H_6Si(OC_2H_4)_3$

$H_3CO(C_2H_4O{-})_{7.5}{-}C_3H_6SHC_3H_6Si(OCH_3)_3$



$H_2C{=}\underset{CH_3}{\underset{|}{C}}{-}\overset{O}{\overset{\|}{C}}OC_3H_6Si[(OC_2H_4{-})_{7.5}{-}OCH_3]_3$

Suitable silanes of formula II useful in the practice of this invention include, by way of example only, the following:

$CH_3Si(OCH_3)_3$, $CH_3CH_2Si(OCH_2CH_3)_3$,

$CH_3CH_2CH_2CH_2Si(OCH_3)_3$, $CH_3CH(CH_3)Si(OCH_3)_3$,

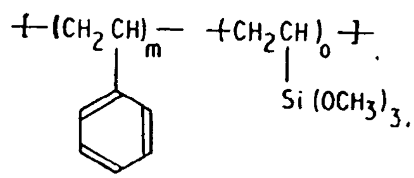
$CH_3(CH_2)_4Si[OCH(CH_3)_2]_3$, $CH_3(CH_2)_6Si(OCH_2CH_3)_3$,

$CH_3(CH_2)_{12}CH(Si(OCH_3)_3)CH_3$, $CH_3(CH_2)_{11}CH(Si(OCH_3)_3)CH_2CH(Si(OCH_3)_3)CH_3$,

$CH_3(CH_2—)_7—Si(OCH_3)_3$, $CH_3(CH_2—)_{17}—Si(OC_2H_5)_3$,

$HOOC(CH_2)_8Si(OCH_3)_3$,

$—[—(—CH_2CH_2—)_m— \quad —(—CH_2CH(C(=O)OH \cdot H_2N(CH_2)_3Si(OCH_2CH_3)_3)—)_o—]—$,



$HOOCCH_2CH_2Si(OCH_2CH_3)_3$,

$H_2N(CH_2)_3Si(OC_2H_5)_3$, $NCCH_2CH_2Si(OCH_2CH_3)_3$,

$H_2N(CH_2)_4Si(OC_2H_5)_3$, $H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3$

$H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2Si(OC_2H_5)_3$,

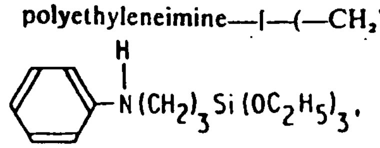
$H_2NC(=O)NHCH_2CH_2CH_2Si(OCH_3)_3$,

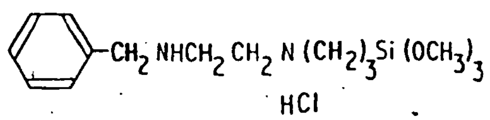
$H_2NC(=O)NHCH_2CH_2N(C(=O)—NH_2)(CH_2)_3Si(OCH_3)_3$,

$H_2NC(=O)—NH(CH_2)_2N(H_2N—C{=}O)—(CH_2)_2—NH(CH_2)_3Si(OCH_3)_3$,

polyethyleneimine—$(—CH_2)_3Si(OCH_3)_3$,

polyethyleneimine—$[—(—CH_2)_3Si(OCH_3)_3]_2$,





$HOCH_2CH_2CH_2Si(OC_2H_5)_3$, $H_2NCH_2Si(OC_2H_5)_3$,

$HOCH_2Si(OCH_3)_3$, $H_2N\underset{CH_3}{\underset{|}{C}}HCH_2Si(OC_2H_5)_3$,

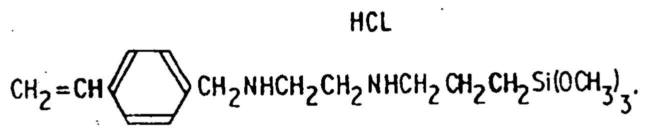
polyazamide- - - -$[CH_2CH_2CH_2Si(OCH_3)_3]_{1-6}$ (see U.S. Patent No. 3,746,748, patented July 17, 1973, for a complete description of silylated polyazamides),

$CH_2{=}C(CH_3)COO(CH_2)_3Si(OCH_3)_3$,

$CH_2{=}C(CH_3)COO(CH_2)_3Si(OCH_2CH_2OCH_3)_3$,

$CH_2{=}CHSi(OCH_3)_3$, $CH_2{=}CHSi(OCH_2CH_2OCH_3)_3$,

$CH_2{=}CHSi(O\overset{O}{\overset{\|}{C}}CH_3)_3$,



$CH_2{=}CH\overset{O}{\overset{\|}{C}}{-}NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3$,

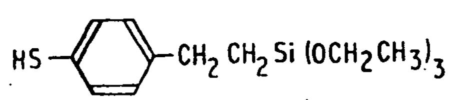
$CH_2{=}CH\overset{O}{\overset{\|}{C}}NH(CH_2)_3Si(OCH_2CH_3)_3$,

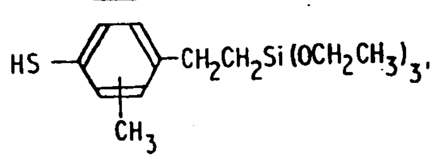
$CH_2{=}CHCH_2Si(OCH_2CH_2OCH_3)_3$,

$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2Si(OCH_3)_3$,

$HSCH_2Si(OCH_3)_3$, $HSCH_2CH_2Si(OCH_2CH_3)_3$,

$HS(CH_2)_3Si(OCH_3)_3$, $HS(CH)_3Si(OCH_2CH_3)_3$,





$HO\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}{-}OCH_2CH_2CH_2Si(OCH_3)_3$,

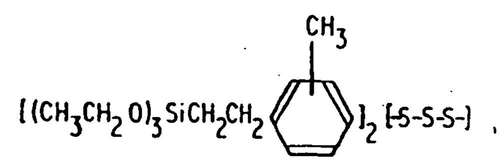
$HSCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}NH(CH_2)_3Si(OCH_2CH_3)_3$,

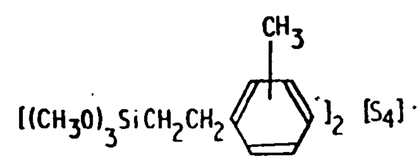
$HOCH_2CH_2CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}NH(CH_2)_3Si(OC_2H_5)_3$,

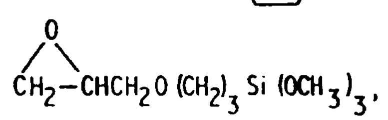
$(CH_3CH_2O)_3SiCH_2CH_2CH_2S—S—S—S—CH_2CH_2CH_2Si(OCH_2CH_3)_3$,

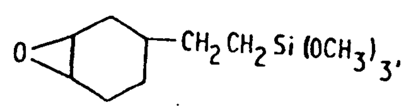
$(CH_3CH_2O)_3SiCH_2CH_2CH_2S—S—S—CH_2CH_2CH_2Si(OCH_2CH_3)_3$,

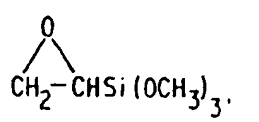
$(CH_3CH_2O)_3Si(CH_2)_3—S—S—(CH_2)_3Si(OCH_2CH_3)_3$,



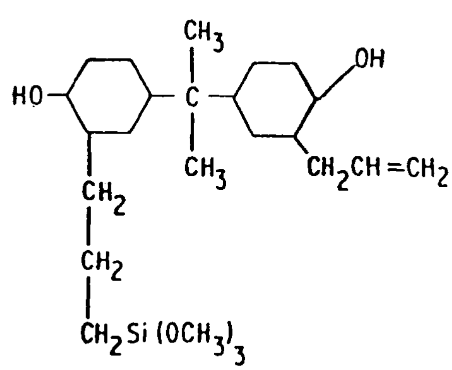








$CH_3CH_2O\overset{\overset{O}{\|}}{C}NH(CH_2)_3Si(OC_2H_6)_3$,



$Si(ONa)_4$, $Si(OCa)_4$,

$CH_3Si(ONa)_3$, $(CH_3CH_2O)_4Si$,

$$((CH_3CH_2O)_3SiO—)_2—(—\underset{\underset{OCH_2CH_3}{|}}{\overset{\overset{OCH_2CH_3}{|}}{Si}}—)_{0-100}—, \text{ and,}$$

For the purpose of this invention a number of terms appearing herein and in the claims which follow should be defined. The terms "particulate inorganic oxide"

and "inorganic oxide particles", are intended to mean any inorganic solid material which possesses either oxygen (chemisorbed or covalently bonded) or hydroxyl (bound or free) at its exposed surface and are intended to include carbon black. In addition, the particulate inorganic oxide is a material which is suitable for use in the various molding or coating processes including injection molding, lamination, transfer molding, compression molding, coating (such as brushing, knife coating, roller coating, silk screen coating and printing and casting. For this reason it is desirably a material which has a limited length or width and in the typical cases does not have a length which, if it is spherical, exceeds 8 inches, and in most cases its length does not exceed 1 inch. Because of the variety of materials that are being attempted to be encompassed by the term particulate inorganic oxide, it is difficult to put a rigid construction on its definition. When the particulate inorganic oxide material is one which is classified as a filler or pigment, as those terms are normally construed, it may or may not be a reinforcing material. In most cases such fillers are irregular in their dimensions, some being elongated such that they have a length which exceeds a defined width. In the main, such inorganic oxides are regarded to be particles and their average particle size varies depending upon how they are to be employed. Some fillers, such as such fumed silicas and carbon black, have an average particle size less than about .1 microns. Other filler materials which may serve the purpose of providing either an abrasive or irregular surface to the composite to which it is being employed will have a much greater particle size, such as being capable of passing only a 10 mesh sieve, U.S. Standard.

The inorganic oxide substrate which can be effectively treated pursuant to this invention by the silane of formula (I) alone or combined with the silane of formula (II), includes those which are normally treated by Coupling Agents. In particular, the invention encompasses the treatment of potentially any inorganic oxide particulate material, as characterized above, which is employed in combination with thermosetting and/or thermoplastic resinous materials. In terms of this invention, the concept of a resinous material, whether it is thermosetting or thermoplastic, does not exclude the possibility that the material is *in situ* formed and therefore is derived from a monomeric material while in contact with an inorganic oxide material which contains or has provided at its surface the silane of formula (I) (or combined with the silane of formula (II)), its hydrolyzate or the condensate of that hydrolyzate. Specific illustrations of suitably employable inorganic oxide materials are, for example, brass (with an oxidized surface), copper metal (oxidized at its surface), aluminum metal (oxidized at its surface), iron or steel (oxidized at its surface), alumina, siliceous materials such as fumed silica, hydrated silica (precipitated silica), silica aerogels, silica xerogels, aluminum silicates, calcium magnesium silicate, asbestos, glass fibers, clays, molecular sieves, Wollastonite, calcium carbonate, carbon black (including lamp black), titanium dioxide (including titanium dioxide which contains HCl soluble alumina and/or silica), calcium sulphate, magnesium sulfate and calcium carbonate containing a silica coating or agglomerated to silica.

Because the aforementioned silanes do not serve a function that is equivalent to the function of a Coupling Agent, it would be improper to characterize them as a member of that class of materials and hence their role in providing strength is not such a factor as to make the size of the particulate inorganic oxide significant in the enjoyment of this invention. For that reason, the silanes of formula (I) are hereinafter to be termed a "Dispersion Promoter", that is, a material which makes the inorganic oxide particulate material more compatible or dispersible within the plastic or resin system in which it is supplied. In one sense the silanes used in this invention serve the function of a surface active agent and in another sense they possess the capacity of enhancing bonding between the inorganic oxide and the resin or plastic in which it is provided. Such bonding is effected by virtue of interface compatibility, and/or by way of associative or hydrogen bonding or through covalent bonding to the extent (generally a minimal factor) that the silane possesses organo functional moieties of the classical kind found in Coupling Agents.

One feature of the Dispersion Promoters of this invention is that they alter the surface characteristics of the inorganic oxide so that they are more readily and more thoroughly dispersed within the resin or plastic in which they are incorporated and this serves to enhance the appearance of the resulting composite and increase the overall strength of the composite when the particulate material employed is one which serves to reinforce the plastic or resin. This invention is concerned with surface treated particulates where the surface treatment is either

the addition of the aforementioned Dispersion Promoters or its hydrolyzate or partial condensate of the hydrolyzate (or the cohydrolyzates or cocondensates thereof) to the surface of the inorganic oxide.

The amount of Dispersion Promoter provided upon the inorganic oxide particles, as characterized herein, is that amount which alters the surface characteristics of the particles so that they are more readily dispersed within the resin or plastic or other medium in which they are incorporated. Typically, the amount of the Dispersion Promoter [or its hydrolyzate or partial condensate of the hydrolyzate (or the cohydrolyzate or condensates thereof as characterized above in regard to the utilization of the silanes of Formula (II))—hereinafter collectively termed "its derivatives"] which is supplied to the inorganic oxide may be as little as 0.25 weight percent to as much as 90 weight percent, based upon the combined weight with the inorganic oxide particles. As a rule, 0.5 to 5 weight percent of the Dispersion Promoter and/or its derivatives is adequate for the purposes of appropriately alterating the surface characteristic of the inorganic oxide particles. However, greater concentrations may be used for purposes which exclude the simple utilization of the so treated inorganic oxide particles in plastics or resins. It has been determined that the so treated inorganic oxide particles when containing excessive amounts of the Dispersion Promoter and its derivatives can be utilized as "dry or semi-dry concentrates". In such a case, the particles are carried for the Dispersion Promoter. In such embodiment of this invention, the particles containing this excessive amount of Dispersion Promoter (the "concentrates") can be mixed within appropriate proportions with untreated inorganic oxide particles and by simply dry blending techniques, the excessive Dispersion Promoter and/or its derivatives is transferred to the untreated particles whereby to effect uniform treatment of the particles with Dispersion Promoter and/or its derivatives. In this sense the concentrate loses its excessive quantity of Dispersion Promoter and/or its derivatives and the total mass of inorganic oxide particle is found to be coated with a relatively uniform concentration of Dispersion Promoter and/or its derivatives.

In some cases, the concentrate may be added directly to the plastic, resin, or other vehicle containing untreated inorganic oxide particles and by the "integral blending" technique the excess Dispersion Promoter and/or its derivatives is transferred to untreated inorganic oxide particles.

The Dispersion Promoter and/or its derivatives may be provided on the inorganic oxide particles by any of the known methods by which Coupling Agents are similarly supplied to particulate surfaces. Thus spraying the Dispersion Promoter while tumbling the particles or mixing the particles in a dilute liquid composition containing the Dispersion Promoter and/or its derivative represent adequate treating procedures.

The plastics and/or resin in which the inorganic oxide particles treated with the Dispersion Promoter and/or its dervatives include essentially any plastic and/or resin. Included in the definition of plastic are rubber compounds. The treated inorganic oxide particles may be supplied to the plastic and/or resin while the same is in any liquid or compoundable form such as a solution, suspension, latex, dispersion, and the like. It makes no difference from the standpoint of this invention whether the plastic contains solvent or nonsolvent, or the solvent is organic or inorganic except, of course, it would not be desirable for any plastic or resin or any of the treated inorganic oxide to employ a solvating or dispersing medium which deleteriously affects the components being blended.

Suitable plastics and resins include, by way of example, thermoplastic and thermosetting resins and rubber compounds (including thermoplastic elastomers). The plastics and resins containing the treated particles of this invention may be employed, for example, for molding (including extrusion, injection, calendering, casting, compression, lamination, and/or transfer molding), coating (including laquers, film bonding coatings and painting), inks, dyes, tints, impregnations, adhesives, caulks, sealants, rubber goods, and cellular products. Thus the choice and use of the plastics and resins with the treated particles of this invention is essentially limitless. For simple illustration purposes, the plastics and resins may be alkyd resins, oil modified alkyd resins, unsaturated polyesters as employed in GRP (glass fiber reinforced thermoset polyester) applications, natural oils, (e.g., linseed, tung, soybean), epoxides, nylons, thermoplastic polyester (e.g., polyethyleneterephthalate, polybutyleneterephthalate), polycarbonates, polyethylenes, polybutylenes, polystyrenes, styrene butadiene copolymers, polypropylenes, ethylene propylene co- and terpolymers, silicone resins and rubbers, SBR rubbers, nitrile rubbers, natural rubbers, acrylics (homopolymers and

copolymers of acrylic acid, acrylates, methacrylates, acrylamides, their salts, hydrohalides, etc.), phenolic resins, polyoxymethylene (homopolymers and copolymers), polyurethanes, polysulfones, polysulfide rubbers, nitrocelluloses, vinyl butyrates, vinyls (vinyl chloride and/or vinyl acetate containing polymers), ethyl cellulose, the cellulose acetates and butyrates, viscose rayon, shellac, waxes and ethylene copolymers (e.g., ethylene-vinyl acetate copolymers, ethylene-acrylic acid copolymers, ethylene-acrylate copolymers).

The inorganic oxide particles treated with the Dispersion Promoter has greater affinity for water and as a consequence they are more readily dispersible in water containing systems. The treated particles are more readily incorporated in and stay dispersed longer and more uniformly in water containing systems such as latexes, water solutions, and water dispersions regardless of whether water is the continuous or discontinuous phase. In addition the Dispersion Promotor enhances, the dispersibility of the treated inorganic oxides in organic solvents ranging from hydrocarbon liquids to highly polar organic liquids. As a result, treated inorganic oxides which possess catalytic activity, such as molecular sieves and bentonite, kieselguhr and Kaolin clays, can be more effectively employed in liquid suspension catalytic chemical reactions. Moreover, Dispersion Promotor treated inorganic oxides particles employed in pharmaceutical applications provide more stable suspensions in liquids lessening hard settling of the particles. For example, Kaolin clay treated with the Dispersion Promotor possesses enhanced dispersibility in water and is less prone to hard settling in a container left standing.

Titanium dioxide is an established pigmentary material which can also be employed as a reinforcing filler, albeit an expensive one. It is commonly made by two processes, the chloride process and the sulfate process. The chloride process is a dry process wherein $TiCl_4$ is oxidized to TiO_2 particles. In the sulfate process titanium sulfate, in solution, is converted by a metathesis reaction to insoluble and particulate titanium dioxide. In both processes, particle formation can be seeded by aluminum compounds. Thereafter, the processes are essentially the same. The TiO_2 particles in a water slurry are put through multiple hydroseparations to separate out the large particles and the further refined pigment in slurry form is passed to a treating tank where the particles may be treated with an aluminum compound and/or silicon compound, such as aluminum triethoxide, sodium aluminate, aluminum trichloride, aluminum sulfate, ethyl silicate, sodium silicate, silicon tetrachloride, trichlorosilane, and the like. By pH adjustment, the pigment is flocculated and precipitated with its coating of alumina and/or silica, or without any coating. It is then made into a filter cake by vacuum drying and further dried in an oven, generally of a vibrating type. The dried pigment is air micronized to break down aggregates of particles. The optimum average particle size can range from 0.05 to .35 microns with a range of 0.1 to 0.25 more preferable.

It is believed that the treatment of titanium oxide with the Dispersion Promoter during the manufacture of the pigment is most desirable. The treatment can take place in the treatment tank before flocculation, or on the filter cake or in the micronizer. "Micronizer" is a Trade Mark. It is believed that treatment prior to the micronizer will serve to minimize aggregation of the particles occurring during the making of the filter cake and/or the drying of it. This provides the advantage of reducing the energy in micronizing, or eliminating it as a step, and/or reducing the loss of fines as occurs during micronizing.

The unsaturated polyesters, as previously described are typically condensation reaction products of an unsaturated polycarboxylic acid and a polyol and generally have an average molecular weight of 500 to 10,000, preferably 1,000 to about 6,000, which based on an acid number, have an acid number less than 100.

Illustrative of suitable unsaturated polycarboxylic acids which are condensed with the polyols to produce the unsaturated polyesters of this invention are those having the formula:

$$C_2H_{2n-2}(COOH)_2$$

wherein n is an integer having a value of 2 to 20 inclusive, preferably 2 to 10 inclusive. Among such acids can be noted fumaric acid, maleic acid, glutaconic acid, citraconic acid, itaconic acid, ethidenemalonic acid, mesaconic acid, allylmalonic acid, propylidenemalonic acid, hydromuconic acid, pyrocinchonic acid, allyl succinic acid, carbocaprolactonic acid, tetraconic acid, xeronic acids, ethylmalonic acid and other like ethylenically unsaturated acids.

Other suitable unsaturated acids include 4 - amyl - 2,5 - heptaldienedioic acid, 3-hexynedioic acid, tetrahydrophthalic acid and 3-carboxy cinnamic acid.

If desired, the acid anhydrides of the acids previously described can be used per se or in admixture with the acids to produce the unsaturated polyesters of this invention.

In addition to the anhydrides of the acids noted above, the following acid anhydrides can also be used; pentenyl succinic anhydride, octenyl succinic anhydride, nonenyl succinic anhydride, chloromaleic anhydride, dichloromaleic anhydride, hexachloroendomethylene tetrahydrophthalic anhydride, commonly referred to as chlorendic anhydride, and the Diels-Alder adducts of maleic acid and alicyclic compounds having conjugated double bonds such as methylbicyclo - [2,2,1] - hepten - 2,3 - dicarboxylic anhydride.

If desired, aromatic polycarboxylic acids, saturated polycarboxylic acids, anhydrides thereof or monocarboxylic acids can be used, in conjunction with the unsaturated polycarboxylic acids or the anhydrides thereof, to produce the unsaturated polyesters.

Illustrative of saturated polycarboxylic or aromatic polycarboxylic acids are, among others, phthalic acid, hexahydrophthalic acid, tetrachlorophthalic acid, succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid and dimethyl succinic acid, as well as derivatives thereof, e.g., chlorinated derivatives.

Among suitable monocarboxylic acids, which usually contain a maximum of twenty-two carbon atoms, are benzoic acid, hexanoic acid, caprylic acid, lauric acid, caproic acid, myristic acid, palmitic acid, stearic acid, arachidic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, eleostearic acid, licanic acid, ricinoleic acid, hexenoic acid, hexadienoic acid and octaneoic acid. It is advantageous for purposes of economy to employ mixtures of acids, particularly those derived from natural sources such as castor oil, dehydrated castor oil, coconut oil, cottonseed oil, linseed oil, oiticica oil, perilla oil, olive oil, safflower oil, sardine oil, soybean oil, tall oil and tung oil (China wood oil).

Illustrative of suitable polyols for purposes of this invention are the dihydric alcohols having the formula:

$$HO{-}({-}CH_2{-})_m{-}\underset{R^2}{\overset{R^1}{C}}{-}({-}CH_2{-})_p{-}OH$$

wherein the sum of m+p is at least 1, preferably 1 to 20 inclusive and R^1 and R^2, which can be the same or different, are hydrogen or alkyl and when alkyl, containing 1 to 20 carbon atoms inclusive. Specific compounds include, among others, ethylene glycol, propylene glycol, butanediol-1,2, butanediol-1,3, butanediol-1,4, hexanediol-1,6, decanediol-1,10, neopentyl glycol and the like.

Also suitable are the ether diols having the general formula:

$$HO{-}({-}C_aH_{2a}O{-})_x{-}H$$

wherein a has a value of at least 1, preferably 2 to 6 inclusive, and x has a value of at least 2, preferably 2 to 10 inclusive. Among compounds falling within the scope of this formula are diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, and the like.

Other suitable polyols are the tetrahydric compounds such as pentaerythritol, dipentaerythritol, diglycerol, pentaglycerol, polyvinyl alcohol and the like.

Preparation of unsaturated polyesters can be carried out by methods well known in the art. As a rule, the condensation reaction is conducted by reacting a mixture containing an unsaturated polycarboxylic acid and a polyol, in an amount of 2 to 15 percent in molar excess with respect to the polycarboxylic acid at temperatures on the order of 160°C. to 250°C., preferably 175°C. to 225°C., to polyesters having an acid number of less than 100, generally 10 to 60, preferably 25 to 50.

The polyesters may contain low profile additives such as described in U.S. Patents 2,528235; 3,261,886; 2,757,160; 3,701,748, 3,549,586; 3,668,178; and 3,718,714.

The polyester may be cured by any of the typical polyester curing agents.

Among suitable peroxides that can be used are those which function as free-radical polymerizaton initiators. Examples of such peroxides are the hydroperoxides such as tert-butyl hydroperoxide, cumene hydroperoxide and paramenthane hydroperoxide; peroxy esters such as di-tert-butyl

diperoxyphthalate or tert-butyl peroxyacetate; alkyl peroxides such as di-tert-butyl peroxide or dibenzyl peroxide; ketone peroxides such as methyl ethyl ketone peroxide or cyclohexanone peroxide; acyl peroxides such as benzoyl peroxide, parachlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide or lauroyl peroxide.

The amount of peroxide used is sufficient to effect a cross-linking or thermosetting of the composition in a relatively short period of time. As a rule the amount used is 0.1 to 5 percent and preferably 0.5 to 2 percent by weight based on the weight of the unsaturated polyester.

Among suitable thickening agents useful in making bulk molding or sheet molding compounds are the oxides and hydroxides of metals of Groups I, II and IV of the Periodic Table (Handbook of Chemistry and Physics, 50th edition). Illustrative of specific oxides and hydroxides of the metals noted are the following: magnesium oxide, calcium oxide, zinc oxide, barium oxide, potassium oxide, magnesium hydroxide, calcium hydroxide and titanium oxide.

The thickening agents are used in amounts of 0.5 to 75 and preferably in amounts of 1 to 5 percent by weight based on the unsaturated polyester.

Fillers which are commonly employed in polyester compositions include, among others, glass fibers, clay, calcium carbonate, silica and hydrated alumina. These materials are generally used in amounts of 20 to 80 percent by weight based on the weight of the polyester resin.

The compositions of this invention can be prepared by mixing the components in a suitable apparatus such as a Cowles (Registered Trade Mark) dissolver, at temperatures on the order of 23°C. to 50°C.

Once formulated, the compositions can be formed into sheets using any suitable apparatus and thereafter molded into thermoset articles of desired shape, particularly thermoset articles such as automobile fenders, dash-boards and the like. The actual molding cycle will, of course, depend upon the exact composition being molded. Suitable molding cycles are conducted at temperatures on the order of 250°F. to 350°F. for periods of time ranging from 0.5 minute to 5 minutes.

The following examples further illustrate the present invention.

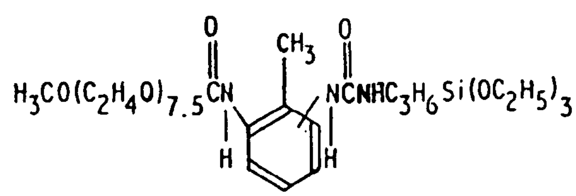
EXAMPLE 1

1135 grams of a precipitated alumina trihydrate, $Al(OH)_3$, of 1.0 micron particle size, such as Hydral™ 710 manufactured by the Aluminum Company of America, were charged to an 8 quart Patterson Kelly™ twin shell blender. With the shell rotating and the intensifier bar operating, 393.3 grams of each silane listed in Table 1 below were fed through the liquid entry port over a period of 15 minutes. The silane charge corresponded to about 25 percent by weight on the completed silane concentrate. An extra 15 grams of silane was included in the charge to compensate for liquid hold-up in the system. After all the silane was added, blending was continued for an additional 15 minutes with the intensifier bar operating.

TABLE 1

Silane	Composition
A	$H_3CO(C_2H_4O)_{7.5}C_3H_6Si(OCH_3)_3$
B	$H_3CO(C_2H_4O)_{11.3}C_3H_6Si(OCH_3)_3$

C

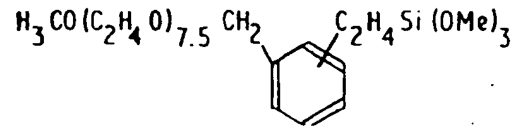


D

$$H_3CO(C_2H_4O)_{7.5}\overset{\displaystyle O}{\overset{\|}{C}}\underset{\underset{\displaystyle H}{|}}{N}\text{—}C_3H_6Si(OC_2H_5)_3$$

E $H_3CO(C_2H_4O)_{7.5}C_3H_6SC_3H_6Si(OCH_3)_3$

TABLE I (cont.)

F 

G $H_2C{=}C(CH_3){-}\overset{O}{\overset{\|}{C}}OC_3H_6Si[(OC_2H_4)_{7.5}OCH_3]_3$

Silane A

Preparation of $CH_3O(C_2H_4O)_{7.5}C_3H_6Si(OCH_3)_3$

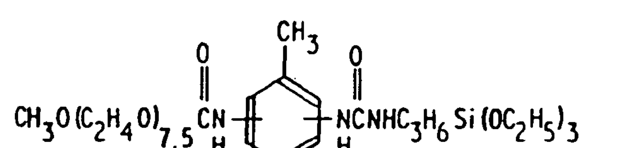
Into a 1 liter 3 necked flask equipped with electric heating mantle, mechanical stirrer, thermometer, liquid dropping funnel and water cooled condenser is charged 398 gms., 1.0 mole, of $CH_3O(C_2H_4O)_{7.5}CH_2CH{=}CH_2$, prepared by reaction of Carbowax® Methoxy Polyethylene Glycol 350 (Made by Union Carbide Corporation, New York, N.Y., U.S.A.) with stoichiometric sodium methoxide and allyl chloride in toluene solution, and 30 parts per million (ppm) of platinum added as a 5% solution of $H_2PtCl_6 \cdot nH_2O$ (40% Pt) in isopropanol. By means of the dropping funnel, 149.0 gms., 1.1. moles, of $HSiCl_3$ is slowly added over a period of 1 hour beginning at 30°C. Heating is continued from 50 to 60°C for 1 hour to complete reaction and excess unreacted $HSiCl_3$ is recovered by distillation to a final pot temperature of 100°C. There results about 533 gms., 1.0 moles, of $CH_3O(C_2H_4O)_{7.5}C_3H_6SiCl_3$ in near quantitative yield, which analyzes 5.5 meg./gm of silyl chloride acidity as measured by titration with a 0.1 N solution of sodium hydroxide. The latter chlorosilane adduct is treated over a period of 2 hours with excess methanol while heating at 70—80°C and maintaining continuous evacuation of by-product hydrogen chloride by means of a water aspirator. There results 520 gms., 1.0 mole, of $CH_3O(C_2H_4O)_{7.5}C_3H_6Si(OCH_3)_3$ in quantitative yield, containing less than 0.1 meg/gm titratable actidity.

Silane B

Preparation of $CH_3O(C_2H_4O)_{113}C_3H_6Si(OCH_3)_3$

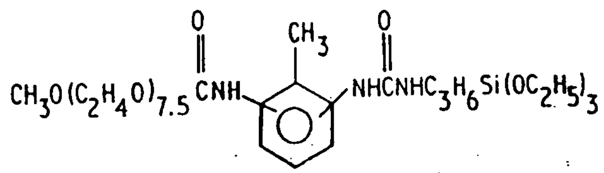
Starting with 250 gms., 0.05 moles of toluene diluted Carbowax Methoxy Polyethylene Glycol 5000 in a 1 liter, 3-necked flask equipped with thermometer, mechanical stirrer, electrical heating mantle and distillation head, successive treatment in the conventional manner with .065 moles of sodium methoxide and 5 gms., 0.65 moles of allyl chloride produces a 50 wt % toluene solution of the corresponding allyl ether capped derivative $CH_3O(C_2H_4O)_{113}CH_2CH{=}CH_2$. Subsequent reaction of 447 gms. of the latter with 5.4 gms., 0.0438 moles, of $HSi(OCH_3)_3$ in the presence of 0.057 gms. of H_2PtCl_6, diluted to 1.09 ml in isopropanol and 0.4 gms. of glacial acetic acid is continued at about 55°C for two hours until complete. Toluene and other volatiles are removed by vacuum stripping to a final temperature of 60°C. The resulting product $CH_3O(C_2H_4O)_{113}C_3H_6Si(OCH_3)_3$ is diluted to 40 wt % solids in toluene.

Silane C

Preparation of  ,

Into a 1 liter, 3-necked flask equipped with thermometer, mechanical stirrer, electric heating mantle and distillation head is charged 150 gms. toluene and 262.5 gms.,0.75 moles, of UCC Carbowax Methoxy Polyethylene Glycol 350. Distillation of 40 gms. of toluene is used to remove traces of contained moisture and thereupon is added 130.6 gms., 0.75 moles, of 80/20 isomeric mixture of 2,4 and 2,6-toluene diisocyanate over a period of 1 hour beginning at about 0°C. Stirring is continued for 1 hour as the reaction mixture slowly exotherms to about 15°C and is finally warmed to about 28°C. By means of a liquid addition funnel is added 165.9 gms.,

0.75 moles, of $NH_2(CH_2)_3Si(OC_2H_5)_3$, and external cooling is provided to maintain a maximum reaction temperature of 25°C. Additional toluene, 100 ml., is added to dissolve resulting solids that form. After stirring 1 hour to complete reaction toluene is removed by vacuum stripping to a final condition of about 1 mm. of mercury pressure at 50°C and the resulting 559 gms., 0.75 moles of



is observed as a waxy solid and is diluted with 50 wt % of anhydrous absolute ethanol.

Silane D

Preparation of $CH_3O(C_2H_4O)_{7.5}\overset{\overset{O}{\|}}{C}NHC_3H_6Si(OC_2H_5)_3$

Into a 1 liter, 3-necked flask equipped as previously described for silane C is charged 297.5 gms., 0.85 moles of Carbowax Methoxy Polyethylene Glycol 350 and 130 gms. of toluene. After heating to 120°C and distilling 40 gms. of toluene to insure removal of trace moisture, 210 gms., 0.85 moles of $O{=}C{=}N(CH_2)_3Si(OC_2H_5)_3$ containing 1 gm. of dissolved dibutyl tin dilaurate is slowly added over 1 hour beginning at 0°C and finally reaching 25°C. Vacuum stripping to 1 mm. mercury pressure at 80°C provides 507 gms. of

$$CH_3O(C_2H_4O)_{7.5}\overset{\overset{O}{\|}}{C}NHC_3H_6Si(OC_2H_5)_3$$

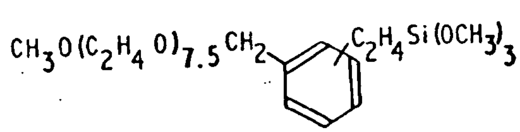
which is subsequently diluted to 75 wt % solids in anhydrous absolute ethanol.

Silane E

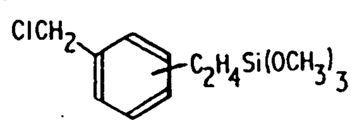
Preparation of $CH_3O(C_2H_4O)_{7.5}C_3H_6SC_3H_6Si(OC_2H_5)_3$

In a 1 liter, 3-necked flask equipped as previously described in Example C is charged 380 gms., 0.95 moles, of allyl ether of Carbowax Methoxy Polyethylene Glycol 350, 186.4 gms., 0.95 moles, of $HS(CH_2)_3Si(OCH_3)_3$ and 2.3 gms. of N,N.-bis - azo - isobutyronitrile. Upon heating the stirred mixture to about 85°C, an exothermic heat rise to 120°C is observed and maintained for about 1 hour. Upon cooling to 25°C there results 566 gms., 0.95 moles of $CH_3O(C_2H_4O)_{7.5}C_3H_6SC_3H_6Si(OCH_3)_3$ which is diluted to 80 wt % solids with anhydrous absolute ethanol.

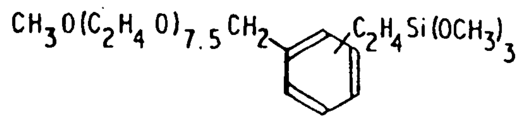
Silane F

Preparation of 

Starting with 315 gms., 0.9 moles of Carbowax Methoxy Polyethylene Glycol 350 and 100 ml. of toluene in much the same equipment set up as previously described for silane B, reaction with 0.9 moles of sodium methoxide by removing methanol provides the sodium salt derivative, $CH_3O(C_2H_4O)_{7.5}Na$. Slow addition of 247.4 gms., 0.9 moles, of



over 1 hour produces an exothermic heat rise from 50° to 90°C and an increasing amount of finely dispersed NaCl. When reaction is complete, cool to 25°C., filter free of salt, remove toluene under vacuum to obtain 527 gms. of



which is diluted to 80 wt % solids with anhydrous absolute ethanol.

Silane G

Preparation of $CH_2{=}C(CH_3)\overset{O}{\overset{\|}{C}}OC_3H_6Si[(OC_2H_4)_{7.5}OCH_3]_3$

Into a liter, 3-necked flask equipped with thermometer, mechanical stirrer, electric heating mantle distillation head and receiver assembly is charged 333 gms., 0.95 moles of Carbowax Methoxy Polyethylene Glycol 350, 236 gms., 0.95 moles, of

$$CH_2{=}C(CH_3)\overset{O}{\overset{\|}{C}}OC_3H_6Si(OCH_3)_3,$$

5.7 gms. of tetra-isopropyl titanate and 0.22 gms. of monomethyl ether of hydroquinone. Heat is applied to maintain a (maximum) reaction temperature of 100°C over a period of 6 hours while retaining 19 gms. of methanol as distillate. Most of the remainder of [30.4 gms. theoretical] methanol is removed by vacuum stripping at 25° to 50°C to a final condition below 1 mm. of mercury pressure. There results 538.6 gms. of

$$CH_2{=}C(CH_3)\overset{O}{\overset{\|}{C}}OC_3H_6Si[(OC_2H_4)_{7.5}OCH_3]_3$$

which is diluted with anhydrous absolute ethanol to 80 wt % solids.

EXAMPLE 2

Separate quantities of 3456 grams of alumina trihydrate of 6 to 9 micron particle size, such as Alcoa C-331 or Great Lakes Foundry Sand GHA-331, were combined with 144 grams of each of the dry silane concentrates described in Example 1 above. The mixtures were each blended for two hours in the twin shell blender and stored for subsequent testing. The average silane concentration in each of the mixtures was 1.0 weight percent.

For comparative purposes, 5, 15 and 25 percent of the 1 micron alumina trihydrate (Hydral 710) without any silane was blended with the 6 to 9 micron alumina trihydrate (GHA-331).

EXAMPLE 3

Separate quantities of 200 grams of Marco™ GR 13021 Polyester Resin* (Sold by W. R. Grace & Co.) were weighed into a one pint tin lined can. 350 grams (175 phr) each of the alumina trihydrate fillers, as characterized in Table 2 below, were slowly added to the resin with gentle hand stirring to promote wetting of the filler by the resin. When all of the filler had been added, the can was covered and mixed with an electrically powered Jiffy™ Mixer Blade (Model LM, Jiffy Mixer Co.) for 15 minutes.

---

*Based upon infrared and nuclear magnetic residence analysis, an idealized segmented chemical representation of this resin, deduced from calculated mole ratios of phthalate, fumarate, 1,3 butane diol and ethylene glycol (as ester groups) is

$$HORO\left[\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}\right]_{7.7}\left[\overset{O}{\overset{\|}{C}}\text{Ø}\overset{O}{\overset{\|}{C}}\right]_{2.3}\left[ORO\right]_{11}H$$

in which ORO diol units=1.8/1.0 mole ratio of 1,3 butane diol/ethylene glycol. The resin contains styrene monomer.

The can of resin-filler mix was conditioned in a constant temperature water bath controlled at 90°F±1°F for two hours. Viscosity of the mix was then determined with a Brookfield™ Synchro-electric Viscometer™ Model HBT, using spindle No. 4 which had also been similarly conditioned for two hours at 90°F.

TABLE 2

Experiment No.	Filler mixed with resin	Viscosity, 10 RPM 10^3 cps
a.	Untreated alumina Trihydrate (GHA-331)	78.4
b.	75 wt % GHA-331/25 wt % Hydral 710 from Example 2	60.0
c.	85 wt % GHA-331/15 wt % Hydral 710 from Example 2	44.0
d.	95 wt % GHA-331/5 wt % Hydral 710 from Example 2	56.0
e.	96 wt % GHA-331/4 wt % Hydral 710 containing 25% Silane A from Example 2	28.8

These data show the well known viscosity lowering effect of filler packing and that a minimum viscosity with untreated Hydral 710 is achieved at 15 percent in a blend with GHA-331.

But the presence of Silane A on the Hydral 710 carrier reduces viscosity by a factor of 2.

EXAMPLE 4

The alumina trihydrate fillers from Example 3 were compared in the following bulk molding compound (BMC) formulation:

Component	Description	Parts by Weight	Grams
Marco™ GR 13021[1]	Unsaturated polyester resin in styrene monomer	80.	200.
Bakelite™ LP-40A[2]	Low profile additive: an acrylic acid modified poly (vinyl acetate) in styrene monomer.	20.	50.
Zinc Stearate	Mold release agent	2.	7.5
Tert butyl perbenzoate	Cross-linking catalyst	1.	2.5
GHA-331[3] (See Table 3 below)	$Al(OH)_3$ 6.5—8.5 avg. particle size	275.	687.5
Glass P-265A[4]×1	1/4" chopped glass strand	76.3	190.7

[1] W. R. Grace & Co., Polyester Division—Marco
[2] Union Carbide Corporation
[3] Great Lakes Foundary Sand Co., Mineral Products Division
[4] Owens-Corning Fiberglas Corporation

The procedure for compounding the formulation was as follows:

The resin, low profile, additive, zinc stearate, and t-butyl perbenzoate were preblended in a one pint wide mouth jar with an air driven "Lightnin" mixer and Jiffy® stirring blade which consisted of a horizontal two bladed propeller with guard ring, and two vertical blades. Care was taken to insure complete dispersion of the zinc stearate in the mutually soluble resin and low profile additive.

The liquid pre-blend was transferred to the (1 gallon) bowl of a Hobart™ N-50 mixer equipped with a dough hook. The 687.5 g of $Al(OH)_3$ was added in each instance in one charge with the mixer stopped. The mixer was then run at speed number one for exactly six minutes. During this period the time for the untreated and treated $Al(OH)_3$ fillers to be completely wetted by and dispersed in the liquid phase was recorded and set forth in Table 3.

TABLE 3

Experiment No.	Alumina Trihydrate	Time for Wet Out and Dispersion in Liquid Phase, seconds
a.	Untreated GHA-331	180
b.	85 wt % Untreated GHA-331/15 wt % Hydral 710 from Example 2	160
c.	96 wt % untreated GHA-331/4 wt % Hydral 710 containing 25% Silane A from Example 2	60

With the mixer stopped, the filled resin was scraped from the sides of the bowl, down into the center, and the first increment of glass charge was added around the wall of the bowl to prevent resin from readhering. The mixer was then run at speed number one and the entire 190.7 gram glass charge added in exactly two minutes. Mixing was continued another two minutes for a total mixing time of four minutes. Commerical practice is to minimize mixing to avoid fiber degradation. The compound was then molded into test plaques.

Test plaques were prepared by charging 400 grams of the above compounds to a single cavity 8"×8"×0.125", chrome plated mold. Top and bottom surfaces were lined with .003" thick Mylar® film. Press cycle was two minutes at 300°F under 40 tons of force.

The resulting plaques were examined visually for uniformity of glass dispersion. The pronounced dark gray swirl pattern with untreated alumina trihydrate is glass. The lighter areas are resin-rich, resulting from incomplete dispersion of glass during mixing in the Hobart and/or "washing" of the resin from the glass as the compoud flowed in the mold. Thus, the less the visual contrast in a plaque, the better the uniformity of glass dispersion.

A visual qualitative assessment of glass dispersion is set forth in Table 4 which is keyed to the experiment numbers of Table 3.

TABLE 4

Experiment Nos.	Alumina Trihydrate	Dispersion Quality
a.	Untreated GHA-331	Fair
b.	85 wt % untreated GHA-331/ 15 wt % Hydral 710 from Example 2	Fair
c.	96 wt % untreated GHA-331/ 4 wt % Hydral 710 containing 25% Silane A from Example 2	Good

The molded plaques were sawed into 3"×0.5"×.161–.233" thick test specimens (depending on plaque thickness). Five specimens pwer plaque were selected randomly for flexure testing by ASTMD 790-71 and the results are shown below:

Alumina Trihydrate	Flexural Strength, psi	Standard Error, %
Untreated GHA-331	8,070	27
96 wt % untreated GHA-331/ 4 wt % Hydral 710 containing 25% Silane A from Example 2	12,334	13

The reduced standard error is additional evidence of improved plaque informity with silane treated alumina trihydrate. The definition for "standard error" can be found in Rickmers et al., *Statistics, An Introduction*, page 22 (1967), published by McGraw-Hill Book Company, New York, N.Y.

EXAMPLE 5

Separate quantities of 1816 grams of GHA-331 were charged to an 8 quart Patterson Kelly Liquid-Solid ("twin-shell") blender. With the blender and intensifier rotating, 150 ml of treating solution of compositions described below were gravity fed, via separatory funnel, to the inlet tube over a period of approximately 15 minutes. The blender and intensifier were allowed to run another 15 minutes to assure adequate liquid-solid dispersion and to minimize agglomerate formation.

The treated contents of the blender were spread to a one inch depth in a 14×18 inch tray and dried for one hour at 100°C.

Each treating solution was prepared by diluting 18.16 grams of one of the silanes described in Example 1 to 150 ml with a 10 volume % water—90 volume % methanol solution which was mixed for about 10 minutes before feeding to the twin shell blender.

EXAMPLE 6

Resin-alumina trihydrate mixtures and viscosity measurements were made as in Example 3, except that a Brookfield Model RVT Viscometer with a No. 6 Spindle was used. The following viscosity data with silane treated filler from Example 5 show the effectiveness of silylated polyethers in viscosity reduction. Comparison of Silane A performance with that of its polyether intermediate shows the contribution of the silane moiety.

Alumina Trihydrate Filler Pretreatment (1 wt %)	Resin-Filler Viscosity at 10 RPM, 10^3 cps Run #1	Run #2
None (Control)	66.7	86.5
Silane A	17.8	—
$H_2C{=}CHCH_2O(C_2H_4O)_{7.5}CH_3$ (used to make A)	50.5	—
Silane B	37	34.0
Silane C	—	64.5
Silane D	—	44.0
Silane E	—	36.5
Silane F	—	38.5
Silane G	—	53.0

EXAMPLE 7

The pretreated alumina trihydrate fillers of Example 5 were compounded into the bulk molding compounds of Example 4. The effectiveness of silanes A—F and the effectiveness of Silane A over its polyether precursor are shown below.

Silane on Alumina Trihydrate	Filler Wetout Time, sec.	Glass Dispersion Uniformity	Flexural Strength psi	Run No.
None	240	Poor	7,570	1
Silane A	90	Good	10,450	1
$H_2C{=}CHCH_2O(C_2H_4)_{7.5}CH_3$	120	Fair	8.625	1
None	165	Poor	8,700	2
Silane B	75	Good	11,300	2
Silane C	140	Poor	10,800	2
Silane D	70	Fair	9,900	2
Silane E	70	Fair	10,000	2
Silane F	85	Good	8,100	2
Silane G	125	Fair	9,800	2

Silane C reduces wet out time and improves flexural strengths. In the case of Silane C the magnitude of wet out time reduction would be greater and glass dispersion would be better if the ethylene oxide chain length were increased to compensate for the hydrophobic effect of the tolyl urethane moiety.

EXAMPLE 8

The dry silane concentrate (DSC) consisted of 25.0 wt. % the silane

composition of one (1) mole of $H_2C{=}C(CH_3)COO(CH_2)_3Si(OCH_3)_3$ and two (2) moles of $(H_3CO)_3Si(CH_2)_3(OC_2H_4)_{7.5}OCH_3$, mole ratio of 1:2, on Hydral 710. This was accomplished by first "fluffing" the Hydral 710 in a twin shell blender which amounted to breaking up any clumps with the high speed intensifier bar and thereby increasing the surface area. The Hydral 710 was then transferred to a Hobart mixing bowl (1 gallon) where the appropriate amount (25 wt %) of the silane composition was applied neat by means of hand spraying and mixing. After complete application of the silane composition, the alumina trihydrate was returned to the twin shell blender to break up any clumps which might have formed. A blend was made by placing, in a twin shell blender, the appropriate amount of DSC and untreated GHA-331 to give a blend containing 1.0 wt % of the silane composition based on total alumina trihydrate weight. The blender was then run for 10 minutes and the alumina trihydrate was removed.

EXAMPLE 9

The following formulation was employed to make a bulk molding compound (BMC):

Component	Parts by Weight	Grams
Marco GR 13021 polyester[1]	80	200
Bakelite LP-40A[2]	20	50
Zinc Stearate	3	7.5
Tertiary butyl perbenzoate	1	2.5
GHA-331[3]	275	687.5
OCF P-265A x 1[4] 1/4" chopped fiberglass strand	76.3	190.7

[1] W. R. Grace & Co., Polyester Division—Marco
[2] Union Carbide Corporation
[3] Great Lakes Foundry Sand Co., Mineral Products Division
[4] Owens-Corning Fiberglass Corporation

Compounding procedure: the polyester resin, low profile additive, zinc stearate and t-butyl perbenzoate were pre-blended in a one pint wide mouth jar by means of an air driven "Lightnin" mixer equipped with a Jiffy® stirring blade consisting of a horizontal two bladed propeller with guard ring and two vertical blades. In the case of integral blend, the silane composition of Example 8 was added at this time. Complete wetting and dispersion of the zinc stearate was the major concern in the blending of these components.

The pre-blend was transferred to the mixing bowl of a Hobart N-50 mixer equipped with a dough hook. In the separate evaluations, untreated alumina trihydrate, pretreated alumina trihydrate and blend of DSC and untreated alumina trihydrate from Example 8 were added, in each case, in one charge (687.5 gm.) to the mixer bowl with the mixer stopped. The DSC and untreated alumina trihydrate which were not dry blended together were added to the liquid phase separately. The DSC was added first and mixed until it was completely wetted at which time the mixer was stopped and the untreated alumina trihydrate was added. Mixing continued until the running time of the mixer totaled six minutes. The mixer was run at speed 1 and six minutes was the standard mixing time for all fillers. During this period, the time for the filler to wet out and disperse in the liquid phase was recorded and set forth in Table 5 below.

TABLE 5

	Untreated	Integral Blend	All GHA-331 Pretreated	DSC Dry-Blended with GHA-331	DSC & GHA-331 added Separately
Viscosity, 10^3 cps Brookfield RVT 10 RPM No. 6 Spindle 32° C.	62.5 75	55 —	42 —	34.5 —	— 46
Time for Resin to Wet Filler (seconds)	180	180	90	90	180 After DSC dispersed, required 120 sec. to wet filler.
Dispersion of glass in filled resin	Worst	Poor	Good	Good	Poor

After the mixing of resin and filler, the sides of the bowl were scraped and the material collected in the center. A portion of the glass charge was spread around the sides of the bowl to stop the resin-filler mix from readhering. The mixer was turned on and run at speed 1 for 4 minutes. The remainder of the glass charge was added within the first 2 minutes of mixing. Composites were molded from the completed compound.

Test composites were prepared by placing 400 grams of bulk molding compound into single cavity, 8"x8"x0.125", chrome plated mold. Mold surfaces were separated from the bulk molding compound by sheets of .003" thick Mylar® film. Composites were pressed under 40 tons of force for 2 minutes at 300°F.

Composites were reduced to 6"x6" by removing the outside inch of material from all sides. Ten 3"x0.5"x.181"–.232" thick test specimens (depending on composite thickness) were cut from each composite.

Five test specimens were selected randomly for dry flexural testing. The remaining five specimens were immersed in boiling water for eight hours. Testing was done in accordance with ASTM 790-71. The results are set forth in Table 7 below.

TABLE 7

	Untreated		Integral Blend		All ATH* Pretreated		DSC Dryblended with ATH*		DSC & ATH* Added Separately	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Flexural strength, psi:	8300	8000	94000	6100	10700	7900	12300	11600	10500	7600
Standard Error, %	18.6	20.7	10.6	12.6	13.8	9.1	5.5	11.5	17.8	18.0
Flexural Modulus, psi:	2.15×10^6	1.90×10^6	2.24×10^6	1.7×10^6	2.23×10^6	1.79×10^6	2.25×10^6	1.79×10^6	2.21×10^6	1.67×10^6
Standard Error, %	8.75	5.35	5.9	8.0	5.8	5.5	4.5	4.0	4.8	4.9

*ATH=alumina trihydrate

EXAMPLE 10

Silane A is shown in the following to be effective in water borne coatings:

Water Reducible Polyester (Water free grind)

Grind Mix (in 1 pint can)	#1 System (parts by weight)	#2 System (parts by weight)
Cargill 7201-80[1]	135.8	135.8
Ti Pure R-960[2] (titanium dioxide)	135.0	135.0
Silicone Emulsifier* (10% in Butyl Cellosolve®)	4.35	4.35
Silane A		1.35
Conditions:		
High Speed Mixer (Saw tooth disc impeller 1—3/4" dia. at 6000 rpm)	5 minutes	5 minutes

[1]Cargill Inc., Chemical Products Div., Minneapolis, Minn.; an oil free polyester, solid content 80% by wt. in normal butanol., visc. (25°C.) Z_2—Z_4 (Gardner Scale), Acid No. of Solution is 40—48 mg of KOH/gm of sample.

[2]E. I. du Pont de Nemours & Co.; rutile grade containing Al_2O_3 and SiO_2 surface treatments.

*$(CH_3)_3Si[(CH_3)_2SiO]_{13}[CH_3SiO((OCH_2CH_2)_{17.5}OCH_3)]_{5.5}Si(CH_3)_3$

Add the following to Grind Mix with mixing

Dimethyl ethanol amine	10.0	10.0
Cymel 303[3]	27.0	27.0
2-ethyl hexanol	0.5	0.5
n-butanol	3.5	3.5
Troy Latex Anti-crater[4]	0.65	0.65
Deionized Water	216.7	216.7

Then applied the resulting coating to 24 gage cold rolled steel Bonderite® 1000 panel—6 mils (wet), 1 mil (dry), air dried for 5 minutes, and baked the panels at 175°C. for 15 min. in a forced circulation oven. The gloss of the baked panel was taken:—

Gloss—60°	76	94
(ASTM-523D) 20°	30	79

[3]American Cyanamid Company; hexamethoxymethylmelamine.

[4]Troy Chemical Corp., Newark, N. J.; proprietary composition.

Hiding power—6 mils (wet) of #2 is equivalent in hiding to 8 mils (wet) of #1 when drawn down on Morest™ hiding power charts (form 05) (Morest Company, Freeport, N.Y.).

By increasing the grinding time from 5 minutes to 15 minutes, the following results were obtained:

	#1 System	#2 System
Gloss—20% (ASTM-523D)	67	79

The use of Silane A is effective in providing high gloss in water reducible enamels. It also reduced the grinding time to obtain high gloss and provided improved hiding power or increased pigment efficiency at the same time.

It was observed that conventionally manufactured aged water reducible enamels tended to produce a reduced gloss on application to panels.

Water Reducible Polyester (Water based grind)

Grind Mix	System (parts by weight) 1	2	3
Ti Pure R-900[1] (titanium dioxide)	177.3		177.3
Treated TiO_2*		179.1	
Silane A	-		1.77
Arolon 465[2] (acid terminated polyester)	60.2	60.2	60.2
Deionized Water	109.9	109.9	109.9
Conditions:			
Pebble Mill (1/2×1/2 inch ceramic cylinders)	20 hrs.	20 hrs.	20 hrs.

[1]E. I. duPont de Nemours & Co., rutile grade containing $A/_2O_3$ surface treatment.

[2]Ashland Chemical Co., Div. of Ashland Oil Inc., Columbus, Ohio—a water reducible oil free polyester; 70 wt % solids in H_2O—monobutyl ether of ethylene glycol mixture.

Then the following was added to the Grind Mix

	1	2	3
Arolon 465[2]	166.7	166.7	166.7
Cymel 301[3]	40.7	40.7	40.7
Butyl Cellosolve®	6.4	6.4	6.4
Silicone Emulsifier[4] (10% in Butyl Cellosolve®)	5.0	5.0	5.0
Deionized Water	4.3	4.3	4.3
Dimethyl ethanol amine	1.0	1.0	1.0
Apply to 1000 Bonderite™ 5 mils (wet), air dry 5 minutes and then bake at 175°C.—20 min.			
Gloss—20° (ASTM 523D)	77	84	83

*R-900 directly treated with a mixture of 0.75 weight % Silane A & 0.25 weight % beta - (3,4 - Epoxycyclohexyl)ethyltrimethoxysilane.

[3]American Cyanamid Company; hexamethoxymethylmelamine.

[4]$(CH_3)_3Si[(CH_3)_2SiO]_{13}[CH_3SiO((OCH_2CH_2)_{17.5}OCH_3)]_{5.5}Si(CH_3)_3$

5 met mils of Systems 2 and 3 are equivalent to 6 mils of System 1 in hiding using Morest charts.

Both the integral blend use of Silane A and the direct application of the silane to dry pigment are effective in improving the gloss and hiding of this type of water reducible polyester.

Latex Coatings

Grind Mix in 500 cc. stainless steel beaker.

	(parts by weight) 1	2	3	4
Distilled Water	200	200	200	200
Potassium tripolyphosphate	8	8	8	
Igepal CA-630[1] (nonionic surfactant)	8	8	8	8
Ethylene glycol	80	80	80	80
Merbac 35[2]	6	6	6	6
Foamaster W-14[3]	6	6	6	6
Ti Pure R-900	840		840	840
Treated TiO_2* (see above)		848		-
Silane A			8.4	8.4
Ammonium Hydroxide (28%)			8	
Citric Acid				10
High Speed Mixer (same as above)				
Grind 15 min. and then added distilled water.	132	132	132	132

[1]GAF Corp. N.Y., N.Y.; octylphenoxypoly(oxyethylene) ethanol. 9 moles ethylene oxide/mole of octyl phenol.

[2]Merck and Co., Rahway, N.J.; benzylbromoacetate.

[3]Diamond Shamrock Chemical Co., Morristown, N.J.; proprietary chemical, antifoam agent.

Mix Slowly				
Above Grind Base	320	320	320	320
Ucar 4358[4]	660	660	660	660
Butyl Carbitol®	16	16	16	16
Dibutyl phthalate	9	9	9	9
Ammonium Hydroxide (28%)	2	2		2
Foamaster W-14 (see above)	1.5	1.5	1.5	1.5
Acrysol G-110 (11%)[5]	22	22	22	22
Ajust to pH 8.6—8.7				
Draw down 5 mils (wet) on glass				
Air Dry				
Gloss—20° (ASTM 523D)	28	29	34	46
60°	67	67	72	76

[4]Union Carbide Corporation Acrylic polymer, 45% solids, 0.15 micron particle size (ave.), Tg 25°C.

[5]Rohm & Haas Co., Phila., Pa.—ammonium polyacrylate solution, thickener, 22% solids in H_2O, pH—≈9.

#3 system and #4 system grinds were adjusted to be on the alkaline and acid side respectively to aid hydrolysis of the silane. All final mixes were adjusted to a pH of 8.6—8.7 with ammonia.

Hiding power chart tests showed 5 mils (wet) draw=downs of systems #2, #3, and #4 to be equivalent to 6 mils (wet) of #1 without silane A, showing improvements in gloss and hiding in the latex systems containing Silane A.

Solvent Based Coatings

Silane A was found to offer gloss and hiding power advantages in solvent base systems. The following systems were prepared by pebble mill.

	(parts by weight)		
	1	2	3
Grind Portion (16 hours)			
Toluene	100	100	100
R-900	100	100	100
Lexinol AC-1 (lecithin)	1.0	1.0	—
Silane A	—	1.0	1.0
Letdown Portion (1 hour)			
VMCC[1] Solution*	320	320	320
7 mil (wet) film on Bonderite® 1000			
24 hr. air dry gloss (ASTM 523D)-60	31	82	67

*VMCC[1]—100 pbw, diisodecylphthalate—20 pbw, methyl isobutyl ketone—150 pbw, toluene—50 pbw.

[1]Union Carbide Corporation; terpolymer of 83 wt % vinyl chloride, 16 wt % vinyl acetate and 1 wt % interpolymerized acid.

Hiding power charts showed that 6 mils of system −2 were equivalent to 7 mils of system −1, therefore Silane A added improvement in gloss and hiding power in solvent systems.

Titanium Dioxide Slurry Treatment

Simulated process treatment of TiO_2 slurries with Silane A resulted in dry product which provided improved gloss and hiding power when evaluated in water reducible polyester enamels.

R-900 and TiO_2 containing 0.3% alumina were evaluated by Silane A treatment in slurry to simulate plant procedures in making TiO_2 pigment where the pigment is treated in a slurry, after hydroseparation of large particles, by coating in the slurry, flocculating the pigment, making a filter cake which is dried and micronized.

The stepwise Silane A procedure used to slurry treat the titanium dioxide was as follows:

To 283 grams of distilled water
add 6 mls 25% (wt) sulfuric acid
add 200 grams of TiO_2 with agitation to pH 3.2
add required amount of Silane A. Mix for 30 min.
Adjust pH to 5.5 with potassium hydroxide solution
Filter on vacuum filter
Wash cake with water to remove salts
Oven dry at 105°C for 1—2 hrs.
Sift dry product thru a 60 mesh screen and evaluate in the following system:

Water Reducible Polyester (Water based grind)

Grind	System (parts by weight)			
	1	2	3	4
Ti Pure R-900 (TiO_2) as received	177.3			
Slurry Treated TiO_2—no silane		177.3		
Slurry Treated TiO_2—1% Silane A			179.1	
Slurry Treated TiO_2—3% Silane A				182.8
Arolon 465	60.2	60.2	60.2	60.2
Deionized Water	109.9	109.9	109.9	109.9
Pebble Mill	4 hrs	4 hrs	4 hrs	4 hrs
Hegman® Grind (ASTM D-1210)	7+	7+	7+	7+
Add the following				
Arolon 465	166.7	166.7	166.7	166.7
Cymel 301	40.7	40.7	40.7	40.7
Butyl Cellosolve	6.4	6.4	6.4	6.4
Silicone Emulsifier (10% in Butyl Cellosolve)®*	5.0	5.0	5.0	5.0
Deionized Water	4.3	4.3	4.3	4.3
Dimethyl ethanol amine	1.0	1.0	1.0	1.0
Apply to 1000 Bonderite 5 mils (wet) then baked at 175°C for 20 min.				
Gloss (ASTM 523D)—20°	75	77	75	80

*See above

Morest hiding power charts show that 5 mils of #4 are equivalent to 6 mils of #1, 2 and 3. Therefore, #4 made with 3% silane slurry treated TiO_2 provides coatings with higher gloss and hiding power. The lack of positive results with #3 indicates that the slurry procedure has to be optimized to quantitatively deposit the silane on the pigment since 1% was effective in previous work where the silane was added directly to the pigment or "in-situ" as a paint additive.

99.7% TiO_2 (0.3% alumina) was treated similarly except that the control was used as received and mix #2 was made with 1% direct treatment for comparison with slurry treated titanium dioxide. The following results were obtained:

Water Reducible Polyester (Water based grind)

Grind	System (parts by weight)			
	1	2	3	4
99.7% TiO_2 (0.3% alumina)	177.3			
Direct Treated TiO_2—1% Silane A		179.1		
Slurry Treated TiO_2—1% Silane A			179.1	
Slurry Treated TiO_2—3% Silane A				182.8
Arolon 465	60.2	60.2	60.2	60.2
Deionized Water	109.9	109.9	109.9	109.9
Pebble Mill	4 hrs	4 hrs	4 hrs	4 hrs
Hegman® Grind	7	7+	7+	7+

Add the following

Arolon 465	166.7	166.7	166.7	166.7
Cymel 301	40.7	40.7	40.7	40.7
Butyl Cellosolve	6.4	6.4	6.4	6.4
Silicone Emulsifier (10% in Butyl Cellosolve)*	5.0	5.0	5.0	5.0
Deionized Water	4.3	4.3	4.3	4.3
Dimethyl ethanol amine	1.0	1.0	1.0	1.0
Apply to 1000 Bonderite 5 mils (wet)				
Bake at 350°F—20 min.				
Gloss—20°	50	81	71	73

*See above.

Hiding power—5 mils of #4 (3% silane) was equivalent to 6 mils of #1, 2 and 3.

The above was repeated by grinding for 12 hrs. to improve dispersion which gave the following results:

Gloss 20°	61	82	78	80

Viscosity of the finished paints were also measured to determine the effect of the silane treatment.

	#1	#2	#3	#4
Viscosity—Brookfield				
6 RPM (cps)	3240	2100	1740	1500
60 RPM (cps)	1152	750	736	650
6/60 viscosity ratio	2.8	2.8	2.4	2.3

As can be seen, the silane treatments effectively reduce the paint viscosity and/or thixotropy (viscosity ratio). This provides the advantage of being able to increase the sprayable solids as well as improve the gloss.

EXAMPLE 11

$CaCO_3$ (Camelwite™[1]: average particle size 99% finer than 10 microns, (wet ground), range 0.3 to 14 microns, wet ground) was treated with 1.0 weight percent Silane A using the method of Example 5. Viscosity of polyester resin containing untreated Camelwite and the above treated Camelwite was measured as in Example 3 except that the filler concentration was 225 parts per 100 parts (by weight) resin.

[1]Sold by H. M. Royal Co., Trenton, N. J.

	Viscosity, 10 RPM 10^3 cps
Camelwite—untreated	44.5
Camelwite treated with Silane A	33.5

The Camelwite was then treated with 1% of the silane composition of Example 8, again using the treating method of Example 5. Bulk Molding Compounds (BMC) were prepared and evaluated as in Example 4 except that the filler concentration in the BMC was 350 parts per 100 parts of resin by weight. The results were:

	Filler Wet-out Time seconds	Glass Dispersion Quality	Flexural Strength, psi
Camelwite, untreated	150	Fair	12,500
Camelwite, treated	130	Good	14,800

EXAMPLE 12

Huber®[1] 35 Clay (water fractionated Georgia Kaolin; 99.7% passes 325 mesh screen; 30—40% finer than 2 microns) was treated with 1% of the silane composition of Example 11 by the method of Example 5 except that 40 pounds of the filler were treated in a larger twin shell blender. Viscosity of polyester resin containing 100 parts by weight of Huber 35 Clay, untreated and treated was determined by the general method of Example 3:

[1]Sold by J. M. Huber Corp., Clay Division, Huber, Ga. 31040

	Viscosity 90°F Brookfield HBT, Spindle TA, 5 RPM 10^6 cps
Huber 35 Clay, untreated	9.9
Huber 35 Clay, treated	6.4

The same treated and untreated Huber 35 Clay was used to prepare the Bulk Molding Compound of Example 4 except that 175 parts (by weight) Clay per 100 parts resin were used.

	Glass Dispersion Quality	Flexural Strength psi Initial	Flexural Strength psi After 8 hour boil	Flexural Modulus 10^6 psi Initial	Flexural Modulus 10^6 psi After 8 hour boil
Huber 35 Clay, Untreated	Poor	13,880	9,700	1.8	1.0
Huber 35 Clay, treated	Good	16,290	12,930	2.0	1.4

EXAMPLE 13

Suzorite™[1] Mica (Phlogopite ore, flake crystal, 1 micron to .75 inch 75/1 aspect ratio) was treated with 1.0% Silane A by the method of Example 5 except that 1.5 pounds of the mica were treated. Viscosity of polyester resin containing 100 parts by weight of treated and untreated mica was compared by the method of Example 3.

[1]Sold by Marrietta Resources International Ltd., Rockville, Md.

	Viscosity, 90°F Brookfield HBT, 10 RPM, Spindle No. 4 10^3 cps
Suzorite Mica, untreated	40.0
Suzorite Mica, treated	26.0

More Suzorite Mica was then treated with 1.0 weight percent of the silane composition of Example 11 by the method of Example 5. Bulk Molding Compounds were prepared and evaluated as in Example 4 except that 69 parts by weight of treated and untreated Mica per 100 parts resin, and 100 parts of glass per 100 parts resin were used.

	Flexural Strength 10^3 psi	Flexural Modulus 10^6 psi
Suzorite Mica, untreated	4,920	1.47
Suzorite Mica, treated	6,690	2.22

EXAMPLE 14

Furnace Creek™[1] Talc (8 micron median particle size, plate structure, low iron) was treated with 1.0 and 0.5 weight percent Silane A by the method of Example 5. Viscosity effects were determined as in Example 3 except that 100 parts filler per 100 parts resin (by weight) were used.

[1]Sold by Cyprus Industrial Minerals Co., Los Angeles, Calif.

	Viscosity 90°F Brookfield HBT, 10 RPM, 10^3 cps
Furnace Creek Talc, untreated	58.0
Furnace Creek Talc treated with 0.5% Silane A	37.0
Furnace Creek Talc treated with 1.0% Silane A	32.0

EXAMPLE 15

Wollastonite[1] F-1 ($CaSiO_3$, 22 micron median particle size 15/1 aspect ratio) was treated with 0.5 weight percent Silane A as in Example 5 except that 2.0 pounds

of filler were charged to the twin shell blender. Viscosity lowering effect in polyester resin was measured as in Example 3 except that 62.5 parts filler per 100 parts (by weight) resin were used.

[1]Sold by Interpace Corp., Willsboro, N.Y.

	Viscosity, 90°F, 10^3 cps Brookfield Model HBT, No. 4 Spindle, 10 RPM
Wollastonite F-1 untreated	42.
Wollastonite F-1 treated with 0.5% silane A	38.

Wollastonite P-1 (9 micron, median particle size, 8/1 aspect ratio) was treated with 1.0 wt % of the silane composition of Example 11 as in Example 5 and compared with untreated Wollastonite P-1 in the polyester Bulk Molding Compound of Example 4 except that 200 parts of the filler were used:

	Glass Dispersion Quality	Flexural Strength, psi	
		Initial	After 8 hour boil
Wollastonite P-1, untreated	Poor	10,500	8,000
Wollastonite P-1, treated	Good	12,600	14,900

EXAMPLE 16

This example shows processing and physical property benefits to treating alumina trihydrate for use in a rigid polyvinyl chloride resin containing formulation of the type used for pipe manufacture.

Separate samples of Alcoa™[1] Hydral 710 (1.0 micron precipitated alumina trihydrate) was treated with Silane A and with the following silane blend, as in Example 3:

Silane A	75 weight percent
$H_2N\overset{\overset{\displaystyle O}{\|}}{C}NHC_3H_6Si(OC_2H_5)_3$ (A-1160)	25 weight percent

Treated and untreated Hydral 710 premixed with the other ingredients shown below were compounded in a Braebender Plasticorder (C. W. Braebender Instruments, Inc., South Hackensack, New Jersey) equipped with a No. 5 mixing head. The cavity was maintained at 200°C and the mixer operated at a constant 60 RPM. Torque was recorded on a scale of 0 to 6000 meter-grams/second. Fluxing time was 4 minutes from the time when torque began to increase. Maximum torque generated is an indication of processability. The lower the peak torque, the better the processing.

Test Plaques were prepared by placing the compound in a 6 inch×6 inch×0.075 inch chrome plated mold preheated to 175°C. Contact pressure was applied for one minute to soften the compound. Force was then increased to 75 tons per 1 minute, maintaining 175°C platten temperature. The press was then cooled 5 minutes by running cold water to the plattens, and the force increased to 125 tons. The composite was removed when the mold had cooled to room temperature.

The composites were tested for tensile stress at yield and failure, modulus, and ultimate elongation and modified Gardner Impact Strength by standard methods.

Formulation	parts by weight
Bakelite® QSAN-7[2] (polyvinylchloride resin powder)	100
Hydral 710 (Alcoa™, 1 micron precipitated alumina trihydrate, treated and untreated	70
Thermolite 73 (M & T Chemicals—Proprietary Stabilizer)	1.0
Calcium Stearate	.85
Acryloid K120ND[3]	1.8
Polyethylene AC629A[4] (Processing Aid)	0.1

[1]Aluminum Company of America, Pittsburgh, Pa.
[2]Union Carbide Corp., New York, N.Y.
[3]Rohm & Haas Company, Philadelphia, Pa.
[4]Allied Chemical Corporation, Morristown, N.J.

Processing characteristics during compound in the Braebender Plasticorder and physical properties of molded plaques containing the three fillers are shown below:

Treatment on Filler	None	1% Silane A	1% (75% Silane A+25% A-1160)
Maximum Compounding Torque: meter-grams	5,640	4,200	4,380
Reduction over no treatment, %	0 (base)	26	22
Tensile Stress, at yield, psi	6,739	5,188	6,393
Tensile Stress, at break, psi	6,739	5,188	6,344
Ultimate Elongation, %	3.4	8.8	4.0
Modulus, 10^3 psi	384	401	439
Modified Gardner Impact, inch-pounds	6.0	>15	>15

The data show that Silane A improves processing, has a plasticizing action, and significantly improves impact strength. The presence of the reactive silane, A-1160, overcomes, the plasticizing effects of Silane A without sacrificing its processing or impact strength improvement contribution.

EXAMPLE 17

Two pounds of pelletized furnace black (Sterling®[1] V-3853) were ground to a powder by mortar and pestle and charged to a 1 gallon jar, which was then rotated on a jar mill for 5 minutes to assure a free flowing powder mass. To achieve a 1.0 weight percent silane concentration based on carbon black weight, 9.08 grams of Silane A were diluted with 10 grams of methanol. About one quarter of this solution was added to the jar which was allowed to rotate five minutes and the remainder of the solution added in quarters with five minute mixing between each increment. When all the solution had been added, the jar was rotated for an additional 20 to 30 minutes. The treated carbon black was then oven dried 2 hours at 100°C.

[1]Sold by Cabot Corp., Boston, Mass.

The effect of the Silane A treatment is shown in the viscosity of polyester resin containing treated and untreated carbon black. The viscosity test of Example 3 was run except that 30 parts of carbon black per 100 of resin was the maximum achievable loading.

Furnace Black	Viscosity: Brookfield HBT, 90°F Spindle No. 4, 10 RPM 10^3 cps
Untreated	48.8
Treated with 1% Silane A	16.0

In our copending British Patent Applications Nos. 40285/77 and 40286/77 (Serial Nos. 1,592,174 and 1,592,387) there are disclosed and claimed compositions

comprising aluminium trihydrate particles containing, on their surfaces, a silane of formula (I). However, no claim is made herein to such compositions.

Subject to the foregoing disclaimer,

WHAT WE CLAIM IS:—

1. A composition comprising inorganic oxide particles (as hereinbefore defined) containing on their surfaces a silane, its hydrolyzates or resulting condensate, which silane has the following general formula:

$$R''—(—OR'—)_a—ORSiX_3 \qquad (I)$$

wherein R can be any divalent organic group which is either oxygen or carbon bonded to the silicon atom; R' is one or more 1,2-alkylene groups each containing at least 2 carbon atoms; R'' is hydrogen, an alkyl group containing 1 to 8 carbon atoms, an acyloxy group containing 2 to 4 carbon atoms or an organofunctional group; X is a hydrolyzable group; and *a* has an average value of 4 to 150.

2. A composition as claimed in claim 1 wherein the amount of silane is from 0.25 to 90 weight percent of the composition.

3. A composition as claimed in claim 2 wherein the amount of the silane is from 0.5 to 5 weight percent of the composition.

4. A composition as claimed in any of claims 1 to 3 wherein R' is one or more 1,2-alkylene groups each containing at least 2 and not more than 4 carbon atoms.

5. A composition as claimed in any of claims 1 to 4 wherein the silane of formula I is coreacted or comixed with a different silane, as encompassed by the following formula:

$$R^3_n(SiX_{4-n})_b$$

or the cohydrolyzate or the cocondensate of such different silane with the silane of formula I, wherein R^3 is an organic radical whose free valence is equal to the value of *b*, X is as defined above, *n* is equal to 0 or 1 and *b* is a positive number.

6. A composition as claimed in any of claims 1 to 5, wherein said inorganic oxide particles are titanium dioxide particles.

7. A resin or plastic composition containing, as a filler, a composition as claimed in any of claims 1 to 5.

8. A composition as claimed in claim 7 wherein said resin is a glass fiber reinforced thermoset polyester.

9. A resin or plastic composition containing, as a filler, a composition as claimed in claim 6.

10. A Composition as claimed in claim 1 and substantially as hereinbefore described with reference to any of Examples 10 to 15 or 17.

W. P. THOMPSON & CO.,
Coopers Building,
Church Street,
Liverpool L1 3AB.
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1981
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.